

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 72

INFLUENCE OF FREQUENCY OF ALTERNATING
OR INFREQUENTLY REVERSED CURRENT
ON ELECTROLYTIC CORROSION

BY

BURTON McCOLLUM, Electrical Engineer
and

G. H. AHLBORN, Assistant Physicist
Bureau of Standards

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By Burton McCollum and G. H. Ahlborn

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INTRODUCTION

This paper describes experimental work done to determine the coefficient of corrosion of iron and lead in soil with varying frequencies of alternating or reversed current with 60 cycles per second as the highest frequency and a two-week period as lowest, some direct-current tests being made as a check on the methods. The results show (1) that a decrease of corrosion occurs with an increase in frequency; (2) that there is a limiting frequency above which practically no corrosion occurs; (3) that the corrosion is practically negligible below a five-minute period; (4) that certain chemicals affect the natural and electrolytic corrosion of the two metals quite differently; (5) that the loss of lead in soil on direct current is about 25 per cent of the theoretical loss; and (6) that alternating or reversed current with as long periods as a day or a week would in the case of iron materially reduce the damage to underground structures.

The importance of these results grows out of the fact that there are large areas in practically every city in which the polarity of the underground pipes reverses with periods ranging from a few seconds to an hour or more, due to the shifting of railway loads. The investigation shows that the corrosion under such conditions is much less than has generally been supposed.

1. DEFINITION

The terms "electrolytic corrosion" and "electrolysis" have been used to designate corrosion caused by the discharge of electric currents which entered the metal from outside sources. In this paper the term "alternating-current electrolysis" applies not only to electrolysis from ordinary alternating currents of commercial frequencies but also to alternating currents of much longer periods, such as several minutes or even a day or longer. Alternating currents of such long periods are very common on portions of underground pipe systems of practically every city, due to the continual shifting of railway loads which causes the pipes within

a large area, commonly called the neutral zone, to continually change their polarity with respect to the earth. In this paper the term "coefficient of corrosion" is frequently used in connection with the corrosion of an anode. This factor is the ratio of the actual corrosion observed to that which would have occurred if all of the electrode reactions determined by Faraday's law had been involved solely in corroding the anode. Thus, if the theoretical corrosion in any case was 100 grams and the observed corrosion 46 grams, the "coefficient of corrosion" would be 0.46. This is sometimes called "efficiency of corrosion."

2. IMPORTANCE AND SCOPE OF THE PRESENT INVESTIGATION

Since most of the electrolysis which occurs is due to stray currents from electric railways, and since only a small percentage of these operate with alternating current, it might seem at first thought that alternating-current electrolysis is of rather infrequent occurrence, and that the problems connected with it do not deserve much attention. However, in addition to the railways which use alternating currents as motive power, such currents often result as an incident of railway operation. These occur not only in the ordinary negative systems of railways mentioned above, as the load shifts from point to point on the track with the movement of the cars, but they occur to a greater extent and in a much larger territory in the case of negative return systems in which insulated negative feeders are used. In such systems the potential differences between pipes and tracks can be greatly reduced, but this is accompanied by a large increase in the area of the so-called neutral zone, in which the polarity of the pipes is continually changing from positive to negative. With certain types of three-wire systems which are now being seriously considered in some places for the prevention of electrolysis, there will be large areas in which the polarity of the pipes will fluctuate between small positive and negative values. It has also been proposed that with the usual type of return that the trolley be made alternately positive and negative on succeeding days or weeks. All of these methods would have the effect of reversing the current flow on underground structures, and the period of the cycle would vary from a few seconds to a day or longer. Moreover, the frequent grounding of 60-cycle lighting circuits permits a certain amount of leakage from those systems, and the corrosion produced, especially in case of accidental grounds on other parts of the system, might be of considerable importance unless it is shown that alternating currents of such frequency do

not give rise to serious corrosion. It is therefore of great practical importance to determine the extent to which periodically reversed currents of these long periods will produce corrosion on subsurface metallic structures.

3. WORK OF PREVIOUS INVESTIGATORS

A number of writers have advanced theories concerning laws governing alternating-current electrolysis and a considerable amount of experimental work has been done with frequencies of 25 to 60 cycles. One writer, discussing the phenomenon from the standpoint of the decomposition of the electrolyte,¹ arrives at certain conclusions: (1) That the amount of chemical decomposition caused by alternating current is less than by direct current; (2) that it is proportional to the electrode current density; (3) that there is a limiting electrode current density below which no decomposition of the electrolyte occurs; (4) that the quantity of corrosion decreases with an increase in the frequency of alternations, and that there is a limiting rapidity of alternation above which there is no decomposition. Conclusions (1) and (4) seem borne out by the experimental work described later.

With reference to the dynamic characteristics of electrolytic cells, several writers have determined by experimental work,² chiefly with the oscillograph, that such cells affect the wave form. As one writer states, the chemical polarization in the cell causes it to behave as a variable condenser with a resistance in parallel and in series.

With a very special set of conditions one experimenter³ has noted an amount of corrosion of the electrodes varying from zero to 35 per cent, with 60-cycle current, and he arrives at the conclusion that the corrosion is practically independent of the current density of the electrodes and temperature; and also that stirring of the solution has no effect. He states that the corrosion does depend on the condition of the electrode surface, but does not attempt to state the principle of this variation.

Experiments of more practical importance to the engineering world were conducted in 1905.⁴ Twenty-five-cycle current was impressed on iron and lead pipes buried in soil and it was found

¹ Dr. Guglielmo Mengarini, *Electrical World*, vol. 18, No. 6, p. 96; Aug. 8, 1891.

² D. Ruchinstein. *Electrolysis with Alternating Current Dynamic Characteristic of an Electrolytic Cell*. *Zeitschrift für Electrochemie*; Dec. 1, 1909; M. LeBlanc. *The emf's of Polarization and Their Measurement by the Oscillograph*. *Deut. Bunsen Gesellschaft*, No. 3. *Alternating Current Electrolysis Use of Oscillograph in Connection with Polarization*. *Zeitschrift für Electrochemie*, 11, p. 707; 1905.

³ G. R. White. *Alternating Current Electrolysis with Cadmium Electrodes*.

⁴ S. M. Kintner. *Alternating-Current Electrolysis*, *Electric Journal*, vol. 2, p. 668; 1905.

that the corrosion was practically the same as that due to the soil alone. No figures of exact losses are given. Alternating current of 25-cycle frequency was impressed on lead and iron plates in salt solution and direct current was impressed on other plates in a similar electrolyte, and it was found that the loss was negligible for the alternating current and very large for the direct current.

Only a year or so later a large number of tests were conducted with 25-cycle, 60-cycle, and direct current on iron and lead plates.⁵ The conditions were varied by using different soils, salts added to soils, varying the temperature and current density. The results show that although there is quite a large variation in the loss with different specimens and that the 25-cycle losses are uniformly greater than the 60-cycle losses, these losses never exceed 1 per cent under normal temperature conditions. The writer notes that some salts—for example, carbonates and alkaline compounds—reduce the electrolytic corrosion of lead plates. He found that an increase of temperature to 40° C increases the corrosion to about 1 per cent. His final conclusions are that alternating-current electrolysis is more irregular than direct-current electrolysis; that nitrates increase corrosion and carbonates generally decrease it, but that the effect is not great enough to be of practical use for protecting lead cables; that lead is more attacked than iron; that the current density does not appreciably affect corrosion except indirectly by increase of temperature; and that the corrosion increases with a decrease in frequency. He attempts to protect lead specimens by making them negative either by connecting them to a zinc plate or with a small direct current, and finds that the loss is considerably less than with the alternating current alone. He finds that a current of 1 per cent of the value of the alternating current is sufficient to give practically complete protection, the corrosion in some instances being less than that due to natural corrosion alone. It will be noted in the above experimental work that the different variables employed, such as current density, chemicals, temperature, etc., do change the action of alternating current, but that in practically no case did the losses exceed 1 per cent. When we consider the large variation of the electrochemical loss produced by direct current under identical conditions, it is evident that differences obtained between 25 and 60 cycle current are practically negligible.

⁵ J. L. R. Hayden, *Alternating-Current Electrolysis*, Trans., A. I. E. E., vol. 26, Part I, p. 201.

Larsen has conducted some experiments on the corrosion effect of reversed currents of very long period using periods of two hours and two days. He found a marked reduction in corrosion, especially on the two-hour period. Prior to the present investigation, however, there have been no published results of tests on reversed currents of periods ranging from a few cycles per second to ten or fifteen minutes per cycle, a range of great practical importance in connection with the electrolysis of underground pipes and cables, as pointed out above.

4. PURPOSE OF THIS PAPER

The data discussed in this paper were obtained as a part of the general investigation of electrolysis conducted by the Bureau of Standards. Its object is not to determine the laws which govern electrolytic corrosion at any one frequency, but to take a standard set of conditions approaching as nearly as possible those existing in practice; that is, wrought iron pipes and lead sheaths imbedded in soil and to determine the corrosion which will occur in the range of frequencies mentioned above, namely, for frequencies ranging from 60 cycles per second to a week or more per cycle. These data will be of material assistance in determining the effectiveness of many of the proposed systems of electrolysis mitigation.

II. DISCUSSION

1. PRELIMINARY EXPERIMENTS ON EFFECT OF CIRCULATION OF ELECTROLYTE

Before beginning the more complete series of tests to determine the effect of change in frequency a number of preliminary experiments were carried out in order to throw light on certain theoretical aspects of the question under consideration. Theoretical considerations led to the belief that the corrosion of frequently reversed currents would be materially increased by rapid circulation of the electrolyte and diminished by conditions which tended to restrict such circulation. If this were true, it was reasoned that in the case of metals buried in soils, in which the circulation of electrolyte is greatly restricted, relatively little corrosion would occur even with periodically reversed currents of long period. Accordingly, a number of experiments were carried out to determine the effect of circulation of the electrolyte on the coefficient of corrosion.

A set of four cells with wrought-iron electrodes and a 1 per cent NaCl solution as the electrolyte were connected in series on 60-cycle current. The electrolyte in cell No. 1 (see Fig. 1) was stirred by a small turbine and in No. 2 the electrolyte was undisturbed; in No. 3 the electrodes were wrapped with filter paper; and in No. 4 the electrolyte was prevented from mechanical circulation by gelatin. Iron electrodes, which were carefully weighed, were connected in the circuits and the current was maintained at about a half ampere for nearly 200 hours. At the end of the run the electrodes were again weighed and the loss determined by difference from the initial weight. Based on the theoretical loss, which would have been about 100 grams, the coefficients of corrosion (see Table

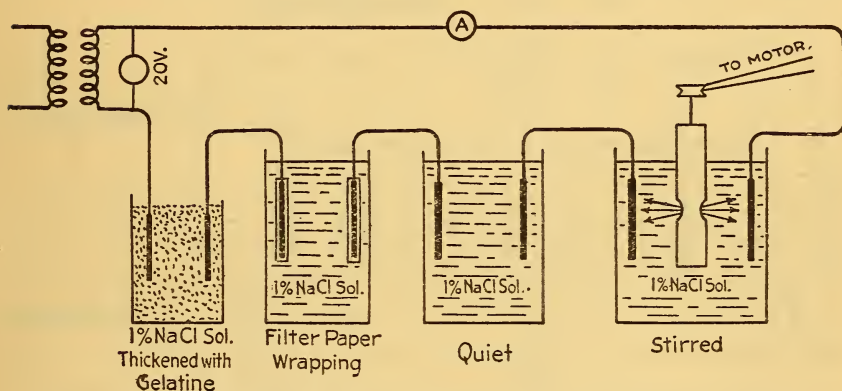


FIG. 1.—First arrangement for testing effect of convection on electrolytic corrosion

1) are 0.0034 for the stirred electrolyte; 0.002 in the stationary solution; 0.0009 when protected by filter paper; and 0.0007 in the gelatin. It seems evident that the chemical action is not as reversible when the electrolyte is in motion about the electrodes as when stationary. In order to determine this effect more exactly a single cell was connected, as shown in Fig. 2. Here there were two electrodes with no current impressed to determine the natural corrosion and two serving as current electrodes. One of these was in the electrolyte stirred by the turbine and the other was wrapped in filter paper and buried in sand saturated with the solution. After correcting for the natural corrosion it was found that the coefficient of corrosion was 0.0004 for the upper electrode and 0.0001 for the lower. The results are shown in Table 1.

TABLE 1

Effects Due to Variations in the Circulation of the Electrolyte

[Sixty-cycle current; wrought-iron electrodes; 1 per cent NaCl solution electrolyte]

State of electrolyte	Total corrosion	Current	Coefficient of corrosion
	Grams	Amp.-hours	
Stirred.....	0.344	96	0.0034
Stationary.....	.202	96	.0020
Filter paper separation.....	.088	96	.0009
Gelatin.....	.074	96	.0007
Stirred.....	.065	160	.0004
Sand saturated.....	.016	160	.0001

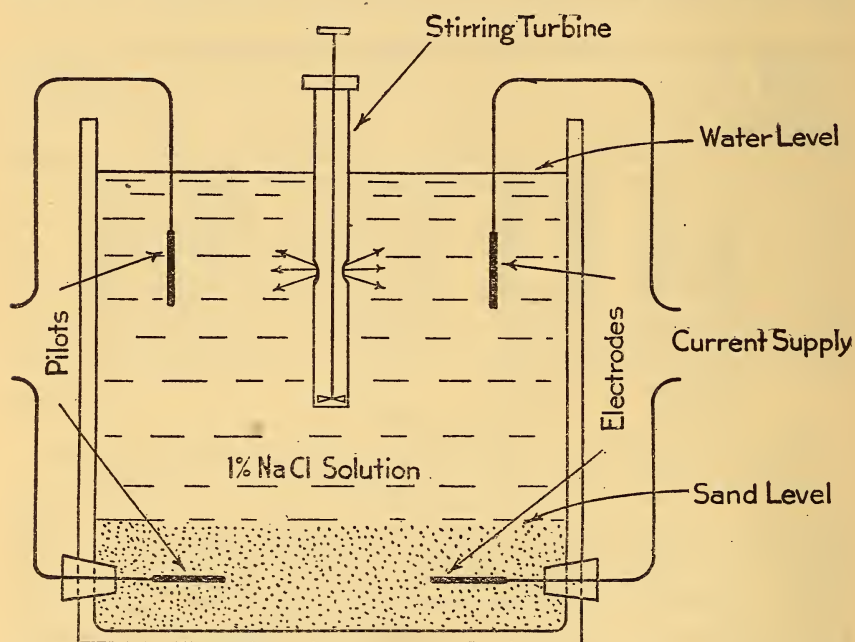


FIG. 2.—Second arrangement for testing effect of convection on electrolytic corrosion

The same type of cell was operated on 20-cycle alternating current with the losses as shown in Table 2.

TABLE 2

Effects due to Variation in the Circulation of the Electrolyte

[Twenty-cycle current; wrought-iron electrodes; 1 per cent NaCl solution electrolyte]

State of electrolyte	Total corrosion	Current	Coefficient of corrosion
	Grams	Amp.-hrs.	
Stirred.....	0.079	144.4	0.0005
Sand saturated.....	.009	144.4	.00006

It will be noted that the corrosion is substantially negligible as in the case of 60 cycles under the same conditions. The same type of cell was placed in a direct-current circuit, which was reversed every 24 hours. As might be expected, the losses were very much greater as shown by Table 3, although the number of ampere-hours was considerably less than that used in the previous experiments.

TABLE 3

Effects due to Variation in the Circulation of the Electrolyte

[Twenty-four-hour reversals; wrought-iron electrodes; 1 per cent NaCl solution electrolyte]

State of electrolyte	Electro-lytic corro-sion	Current	Coefficient of corro-sion
	Grams	Amp.-hrs.	
Stirred.....	45.45	97.1	0.45
Sand saturated.....	32.45	97.1	.32

The electrode surrounded by the moving solution had a loss corresponding to a coefficient of corrosion of 0.45, while the other gave 0.32, the difference due to stirring thus being even more evident on the slow reversals than on the high frequencies. If only the current discharged by each electrode as anode were considered, the coefficient of corrosion in the stirred solution was 0.90, and that in the confined electrolyte was 64 per cent.

The foregoing results show that the free circulation of the electrolyte has a pronounced effect on the coefficient of corrosion, and that this effect is greater the lower the frequency of alternation of the current. They show that the low corrosion coefficient on alternating current is not determined solely by the speed of the reactions and the frequency of alternations. A more probable explanation is that the corrosion during any half cycle in which the electrode is anode takes place nearly in accordance with Faraday's law, as in the case of direct current, but that during the succeeding half cycle when the electrode is cathode a large part of the corroded metal is electroplated back on the electrode. The increased corrosion due to circulation of the electrolyte would be expected under this theory, since the convection currents in the liquid would carry away from the electrode surface a part of the metal that has been corroded during the half of the cycle when the electrode is anode, thus preventing as complete a redeposition during the succeeding half cycle as would otherwise occur. In particular these convection currents in the electrolyte would bring

into contact with the metallic ions, oxygen or other chemicals which would tend to form insoluble compounds, thus rendering the corrosive process irreversible.

Accepting the above theory we would expect that in the case of iron or lead buried in soils, in which circulation of the electrolyte is greatly restricted, the corrosive process would be in large degree reversible even with much longer periods of reversal than in the case of liquid electrolytes, and it seemed possible that this condition might prevail even where the period of the cycle is several

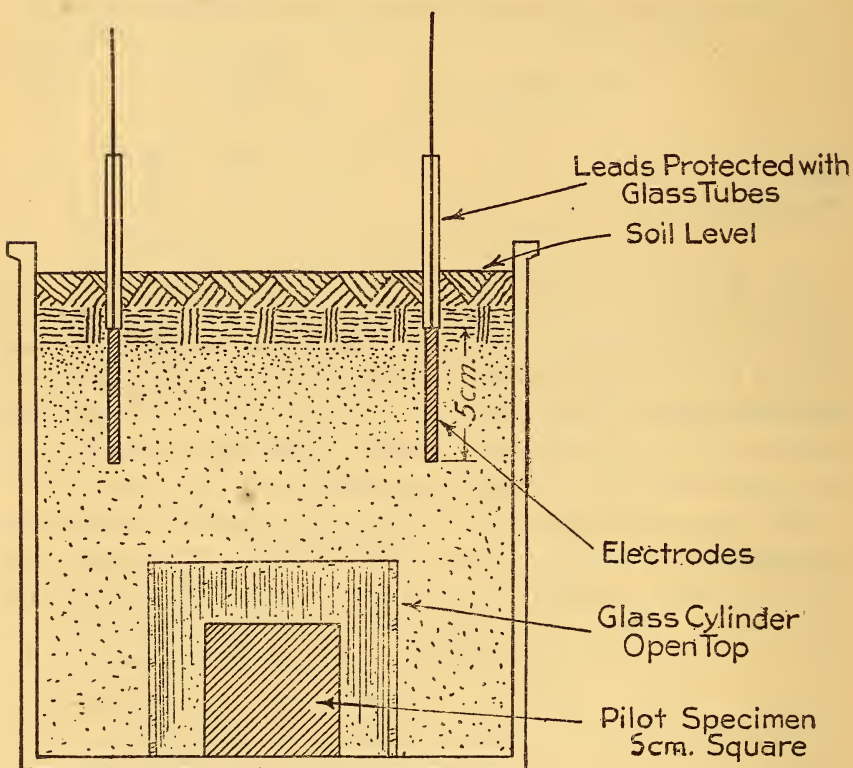


FIG. 3.—Arrangement of electrodes and check specimen in A. C. electrolysis tests

minutes or longer, as in the case of the polarity of buried pipes in many localities as mentioned above. This was found to be actually the case, as the following-described experiments show.

2. COMPLETE SERIES OF TESTS

(a) **Arrangements.**—With the results of the above experiments in view, a more complete series of tests was planned. Since there is considerable variation among individual specimens, it was recognized that quite a number of specimens under each frequency

would be necessary in order to get a fair average. The specimens were arranged in cells having two current-carrying electrodes and one specimen subjected only to soil corrosion, this specimen being protected from the flow of current by a glass cylinder, as shown in Fig. 3. In a few cases the effect of adding sodium carbonate to the soil was studied. For convenience, the greater part of the tests were made in jars in the laboratory, but a number were made in specimens buried in soil out of doors, in order to check the results obtained in the laboratory. The agreement between the results under the two conditions was found to be satisfactory. The entire series is outlined in Table 4 below.

TABLE 4
Summary of Tests

(a) DIMENSIONS OF ELECTRODES

Electrodes	Indoor	Outdoor
	cm	cm
Iron.....	5 by 5 by 0.5	20 by 20 by 0.2
Lead.....	5 by 5 by 0.2	15 by 15 by 0.4

(b) FREQUENCIES USED AND NUMBER OF SPECIMENS USED FOR BOTH IRON AND LEAD

Frequency of reversal	Number of indoor specimens		Outdoor tests
	Natural soil	Soil with Na ₂ CO ₃	
60 cycles per second.....	18	18	3 large; iron only.
15 cycles per second.....	18		
1-second cycle.....	18	18	3 large; iron only.
6-second cycle.....	18		
1-minute cycle.....	18		
5-minute cycle.....	18		
10-minute cycle.....	18	18	
1-hour cycle.....	18		
2-day cycle.....	18		
2-week cycle.....	18	18	
Direct current.....	18	18	3
Total.....	198	90	9 large.

Grand total for iron..... 297
Grand total for lead..... 291
Grand total for all tests..... 588

(b) **Electrolyte.**—In determining the coefficient of corrosion with different frequencies of current reversal it is desirable to simulate operating conditions as nearly as is feasible in a complete

and general test. For this reason soil was selected as the electrolytic medium rather than water, which contains the soluble constituents found to exist in soil by chemical analysis. Conditions of circulation of the electrolyte and the electrolytic transfer in it are very different than in soil. The soil used was natural soil near the Bureau of Standards, a light clay having a resistance of 8000 ohms per centimeter cube at approximate saturation. It will support a good vegetable growth and is a fairly normal soil. Soil from the same locality was used in the experiments described in a previous Bureau of Standards' report⁶ and a coefficient of corrosion of 100 obtained on iron at a definite current density.

(c) **Conditions of the Tests.**—Some of the tests were run in the soil out of doors with natural drainage and aeration. Although it was considered very desirable to make a number of such tests, to run a complete series in outside soil would have been very difficult on account of interference by weather, difficulty of getting electrical connections to many electrolytic cells, and especially the insulating of the various sets from each other, which would be necessary in order to determine the current actually entering or leaving each specimen. The cells used in the inside laboratory tests were 1 gallon (3.8 liters) earthenware jars filled with soil to about 3 cm from the top (about 3 kg), kept practically saturated by adding a quantity of distilled water every day. The tops were left open that evaporation and aeration might go on in a normal way.

(d) **Chemicals.**—Since some soils vary widely in chemical constituents, and these may have a pronounced effect on the rate of corrosion, it seems desirable to vary those constituents in the soil which may be expected to affect the corrosion. As indicated by preliminary tests, sodium carbonate (Na_2CO_3) has a very considerable effect on the electrolytic corrosion of both iron and lead; moreover, sodium is a common element in soil, as are carbonates, and this combination is quite soluble, which makes it a satisfactory compound to use in the soil, 0.5 per cent being added to certain cells, as shown in Table 4.

(e) **Electrodes.**—Since iron and lead are the two metals commonly serving as underground electrical conductors exposed to soil they were selected as the materials for specimens in these tests. The above-mentioned report shows that the corrosion of different kinds of iron does not differ by large percentages under the conditions of these tests, and since "American iron," which is Besse-

⁶ McCollum and Logan, *Electrolytic Corrosion of Iron in Soils*, Technologic Paper No. 25.

mer-process steel, is obtainable in convenient form, it was adopted. This material was fine-grained and quite pure, having about one-tenth per cent carbon and no slag. The lead was commercially pure and on analysis was found to contain traces of tin or antimony. Indoor specimens were 5 by 5 cm square, the iron being about 0.5 cm thick and the lead 0.2 cm thick. The outdoor iron specimens were 20 cm square and about 0.2 cm thick.

The mill scale and oxide left on the materials in the process of manufacture was not removed, since it was felt that with alternating current the surface might affect the corrosion considerably more than with direct current. The leading-in wire was soldered to a corner of each specimen and a number stamped on the same corner. It was then weighed and a glass tube put over the lead and the tube was then sealed with pitch and the lead attachment and number covered with the same material. This type of connection failed in very few instances, due to corrosion, and the tube and pitch were easily removed with toluol before the specimen was reweighed.

(f) **Frequency.**—In determining the frequency of reversal of current two things must be considered: First, the frequencies found in practice; and, second, the completeness of the series, so that a suitable curve could be obtained showing the relation between the corrosion coefficients and the frequency of reversal of current. The standard lighting frequency 60 cycles is available, and 15 cycle was adopted as about the lowest frequency proposed for power work. To obtain the slow reversals a reversing commutator machine was built which is described in detail later. It gave periods of 1 second, 6 seconds, 1 minute, 5 minutes, 10 minutes, and 1 hour. The short periods of reversal were adopted because reversals of polarity of such frequencies commonly occur in the usual operation of a street-railway system as pointed out above. Daily and weekly reversals and direct-current tests were also made. The direct-current specimens serve as a check on the theoretical coefficient of corrosion.

(g) **Current Density.**—The density of the current flowing to or from the plates was intended to be such as to produce approximately 1.00 as the coefficient of corrosion with direct-current electrolysis. This is shown in Technologic Paper No. 25 of the Bureau of Standards above referred to, to be about 0.5 milliamperes per square centimeter for iron, and approximately this value was used on both the indoor and outdoor specimens.

(h) **Length of Run.**—The tests were continued until enough effect was produced to permit of accurate determination of the differences in weight of the specimens before and after test. It was also intended that one of the tests should be continued until a state of equilibrium was reached in the cell; that is, until the rate of corrosion was not changing rapidly as might be the case during the first few cycles of current. Moreover, the cells should not be run to an exhaustion of the soluble chemicals, their concentration being probably closely related to the amount and rate of corrosion occurring on the electrodes. Since the current density is the same in all cases, this rate will depend on the frequency of reversal, and since the coefficient of corrosion is less on the higher frequencies, these must run fully as long as the lower frequencies in order to obtain sufficient weight differences. A period of 15 to 20 days has been found to produce sufficient differences in weight, and no indication that the composition of the soil except that very close to the electrodes had been changed decidedly.

(i) **Accidental Variables.**—Other possible variables that have received attention during the experiments were maintained as nearly constant as possible. The temperature did not vary widely from 20°, there being very little heating by the current at the voltage and current density used. The depth was maintained about 10 cm below the surface in the indoor tests and about 40 cm in those outside the laboratory.

(j) **Cleaning Electrodes.**—After each run was completed it was necessary to remove the end products of the corrosion process, and since they adhered firmly in some cases special methods were necessary. Iron specimens were cleaned by making them cathode on a 10-volt circuit in a 2 per cent sulphuric acid solution, as described in Technologic Paper No. 25 of the Bureau of Standards. This was found to be very effective and did not attack the iron enough to show on the balances used. The lead specimens were cleaned by immersing them in a solution containing 5 per cent oxalic acid and 1½ per cent of nitric acid. The corrosion products became lead oxalate—a white flocculent substance which was easily removed by brushing. It was found in some cases where the amount of corrosion was large and adhered very firmly that this process was very slow and did not remove the corroded products entirely. Unoxidized specimens weighed before and after immersion in this lead-cleaning solution were found to have lost less than 5 milligrams, the limit of the balances used.

3. EQUIPMENT

(a) **Current Sources.**—Sixty-cycle current was obtained from the city power mains while the 15-cycle current came from a small inverted rotary converter. Transformers were used in both circuits to raise the voltage so that a number of cells could be operated in series and so that the primary side would be clear of ground. For the slower reversals of current on the indoor tests power was obtained from the regular three-wire lighting bus bar and commutated by the machine described below. For the outdoor tests for slower reversals and for direct current a small motor-generator set was used. A no-current indicator was used on the alternating-current circuits while a recorder showed what had occurred on the direct-current circuit and those of long period at all times.

(b) **Commutating Machine.**—The commutating machine through which the intermediate frequencies were obtained consisted of a series of six commutators each having four brushes and two equal semicircular commutator segments, giving two complete cycles per revolution, driven by gears having such ratios that with the first or highest speed commutator rotating once in two seconds the succeeding commutators made complete current cycles in 6 seconds, 1 minute, 5 minutes, 10 minutes, and 1 hour. This machine was driven by a constant-speed motor.

(c) **Resistance.**—In order to obtain the correct current density discharged from the electrodes the resistance of the circuits had to be varied. This was done in part by placing cells in series in groups and paralleling these groups. Rheostats or tungsten lamps were then used to get final adjustments, but no great effort was made to keep the current discharge at exactly 0.5 milliamperes per square centimeter since a small variation in current density does not affect the rate of corrosion. Tungsten lamps with their high positive temperature coefficient are very satisfactory for use in such circuits, since within a certain range they tend to automatically maintain the current at a constant value.

(d) **Current Measurements.**—Observations of current were made every day, and more frequently when the current values were changing appreciably. A standard millammeter having a resistance of 0.34 ohm was used for all frequencies above one second. For alternating-current measurements a thermoammeter consisting of a heating element, thermocouple, and millivoltmeter was used. The resistance of this meter amounted to about 7 ohms

and was noninductive. When this meter was introduced in circuits, the effect on the current flow was negligible because of the high resistance of the circuits and it was very easy to correct for this small noninductive resistance by inserting an equal amount in each circuit when the meter was not in use. This meter was used to measure larger currents in the outdoor specimens by means of a shunt. A suitable ampere-hour meter was not available.

4. CORRECTION AND REDUCTION FACTORS

Since chemical corrosion, according to Faraday's law, is proportional to the average current flowing, and since all alternating-current values as observed are effective values rather than average, the current flow has been corrected by dividing the same by 1.11, the ratio between effective and average values of sine-wave current. Since the current flowing with the longer time reversals is controlled by a commutating machine or switch the wave is flat-topped and no such correction is necessary. However, the current was off when controlled by the commutating machine 6 or 7 per cent of the time and this correction was applied to all such values. In order to correct any error due to a possible difference in the length of succeeding one-half cycles, the connections to the commutator controlling each test were reversed at regular intervals, e. g., the 1-second commutator was reversed through the 10-minute commutator and the 1-hour one by a switch every 24 hours. In calculating the theoretical amount of corrosion, the corrosion products of both iron and lead were taken to be divalent and the quantity corroded per ampere-hour is then 1.04 grams for iron and 3.86 grams for lead.

5. ACCURACY OF RESULTS

The accuracy which can be obtained in corrosion experiments of this kind is limited by a number of factors: First, the consistency of the corrosion action itself, which it has been found may vary within wide limits under apparently similar conditions; and second, the limits of measurement. The electrical measurements are correct to about 1 per cent while the time measurements are not in error more than a half per cent. The error due to weighing of single specimens was small, since it was carried to the fourth or fifth place, but in some cases the losses were small and this difference was correct to only the second or third place. This is true of practically all pilot specimens which were subjected only to natural corrosion. Therefore it is evident that the accu-

racy of the results is greater when the amount of corrosion is large. The combined accuracy of all measurements was much greater than the consistency to be expected in the corrosive processes.

6. DESCRIPTION OF EACH RUN

The above description of the general condition of the tests is intended to apply to all the following data, and it will be necessary to describe each run only very briefly, deferring until later the presentation of the results.

(a) **Sixty-Cycle Tests.**—The 60-cycle tests were run with both iron and lead specimens for the indoor tests and iron for the outdoor tests. Both natural soil and soil with 0.5 per cent sodium carbonate added were used for the indoor tests. It will be noted from the tables presented below in this as well as in other runs that the natural corrosion losses have been rather large on the iron pilot specimens. This is due to the fact that the mill scale was not removed from these specimens before the tests were started and that the cleaning process removed this scale as well as the oxide that was formed during the test. This rather obscures the comparative effect of natural soil and sodium carbonate, but it is still evident, as in the earlier tests, that the natural corrosion loss of iron is greater in natural soil while the electrolytic corrosion is greater in the chemical soil. In fact, in almost every instance the natural loss was greater than the electrolytic loss in the natural soil, and in 5 of the 12 specimens also in the chemical soil.

With the three large specimens used in the outdoor tests the natural loss was considerably less than the electrolytic loss, and the coefficient of corrosion is only slightly less than 1 per cent.

(b) **Fifteen-Cycle Tests.**—The 15-cycle tests were run with lead and iron in soil only, these cells being in series with about 310 volts, giving about 25 volts per cell. In every case except four iron electrodes the electrolytic losses were all greater than the natural corrosion in the same cells.

(c) **One-Second Period.**—Iron and lead specimens in both normal soil and soil with sodium carbonate were used in the tests with 1-second period, the cells being divided into four groups of three each in series. In two cases the iron electrodes lost more than the pilot specimens, but on the average the losses were greater than in the preceding tests. Iron specimens were placed in outdoor soil for these tests, and in this instance the natural corrosion is unusually high because the specimens were left in the ground without current for a considerable time.

(d) **Six-Second Period.**—Normal soil alone was used in these tests, there being three groups of cells and four cells in each group. Approximately 12.5 volts existed across each cell in order to maintain the current at about 30 milliamperes or 0.5 milliampere per square centimeter.

(e) **One-Minute Period.**—In the one-minute reversals iron and lead electrodes were used in natural soil connected in three groups of four cells each. Approximately 9 volts were maintained across the cells containing the iron electrodes and 14 volts on the lead electrodes. In case of the iron electrodes there was a consistently greater loss on the odd electrode than on the even, the reason for which is not altogether evident since no such consistency exists on the lead specimens; and as the two sets were in series, it is therefore not due to unbalanced or unequal half cycles.

(f) **Ten-Minute Period.**—Both iron and lead specimens in natural soil and soil containing sodium carbonate were used in the 10-minute period tests. The cells were divided into four groups of six each. It will be noted that the corrosion of iron in natural soil is here greater than in the chemical soil, and the reverse is the case with the lead specimens.

(g) **One-Hour Period.**—Only natural soil was used in the one-hour reversals, about 15 volts being impressed on each pair of electrodes.

(h) **Forty-Eight-Hour Period.**—Natural soil alone was used in the daily reversals (48-hour period) with iron and lead electrodes, the entire set being in series on 240 volts. The iron specimens had a voltage of about 15 volts on each pair and the lead electrodes about 13 volts. In the case of the iron specimens, the odd and even specimens, or those anode first or anode last in the test show no great or consistent difference as was noted in the preliminary tests, and the lead specimens show an opposite effect from that noted at that time; that is, the electrodes which were anode during the first half cycle have lost more than those which were cathode initially.

(i) **Weekly Reversals.**—Both natural soil and soil containing sodium carbonate were used in the weekly reversals (two-week period) and the entire set was connected in series on 240 volts. The voltage across the iron specimen cells in the natural soil was about 15 volts per cell and about 9 volts in the chemical soil. With the lead electrodes the average voltage was less than 12 across each cell in the natural soil and less than 4 in the chemical soil.

(j) **Direct-Current Tests.**—The direct-current tests were carried on with iron and lead specimens both indoors and outdoors, and in the indoor tests with sodium carbonate in the soil as well as natural soil. The indoor cells were connected in four groups of six each with 230 volts impressed on them. The ampere-hours varied in the different groups from 8 to 12. With the iron specimens the anode losses are large, the coefficient of corrosion being approximate unity, while the cathode specimens lost less than the pilot specimens, evidently because of the protective effect of the current. In the lead specimens, however, the anode losses are far below what might be theoretically expected, while the cathodes lost less in the natural soil than the pilot specimens, but more in the soil containing sodium carbonate. This is due not so much to an increased electrolytic loss in the chemical soil, but to a greatly decreased natural loss. Since the loss in the lead specimens was so much less than might be expected, another set was run under practically the same conditions but with the current maintained more closely at 0.5 milliamperes per square centimeter. These results, however, corroborate the work previously done. The outdoor tests were conducted on both lead and iron with the large plates mentioned above. The protective effect of the current is noted again on the iron specimens. In the lead specimens 12 anodes were used, the lead in this case being sections of lead-sheath cable, 6 of which contained about 1 per cent antimony while the other 6 contained only traces of tin and antimony. Two pilot specimens of each composition were used. These tests further corroborated the results of the indoor tests in that the coefficient of corrosion of lead on direct current was low.

7. DISCUSSION OF RESULTS

Tables containing the summary of the results of the above-mentioned tests are given below. These tables are arranged in halves with losses in grams above and the coefficient of corrosion below with the frequency or period of reversal in the first column, the average loss of six specimens in each of the three succeeding columns (the first being the odd numbered electrodes and the second the even numbered electrodes and the third the pilot specimens). From these are calculated the electrolytic loss of odd or even electrodes shown in the fifth and sixth columns, and the seventh column contains the average electrolytic loss of all electrodes. Below the frequency is repeated and the next column contains the average quantity of electricity in ampere-hours flow-

ing through the specimens. Following this are four columns giving the coefficient of corrosion. The coefficients of corrosion of the odd electrodes and even electrodes are first given, then the coefficient of corrosion based on one-half the current or that while each electrode was positive, and last that based on the average loss and the total current through the cells. Since it is difficult to draw any conclusions from the electrode losses shown without also considering the ampere-hours, the coefficients of corrosion will give us the best idea of results, and these are shown in both the tables and curves.

(a) **Indoor Tests—Iron in Normal Soil.**—In Table 5 a summary of the results obtained using iron electrodes in indoor cells containing normal soil is given.

TABLE 5

Summary of Alternating Current Electrolysis Tests—I

[Variable, frequency of reversal; indoor tests; iron electrodes; soil electrolyte]

Period of cycle	Total loss			Electrolytic loss		
	Odd electrodes	Even electrodes	Pilot	Odd electrodes	Even electrodes	Average
	Grams	Grams	Grams	Grams	Grams	Grams
60-cycle.....	1.480	1.289	1.645	-0.165	-0.356	-0.261
15-cycle.....	1.036	.862	.834	+ .202	+ .028	+ .115
1-second.....	1.064	1.190	.640	.424	.550	.488
6-second.....	.960	1.046	.566	.394	.480	.437
1-minute.....	2.024	2.077	1.203	.821	.874	.848
5-minute.....	1.907	1.398	.748	1.159	.650	.904
10-minute.....	2.522	2.252	.901	1.621	1.351	1.486
1-hour.....	3.134	2.941	1.165	1.969	1.776	1.872
2-day.....	5.490	5.124	1.130	4.360	3.994	4.177
2-week.....	8.349	9.680	1.387	6.962	8.293	7.627
Direct-current.....	9.697	.139	1.023	8.674

Period of cycle	Current discharge (amp. hours)	Coefficient of corrosion			
		Odd electrodes	Even electrodes	On basis of anodic current	On basis of total current
60-cycle.....	16.05	-0.0198	-0.043	-0.031	-0.0156
15-cycle.....	13.32	+ .0292	+ .0004	+ .016	+ .008
1-second.....	17.99	.045	.059	.046	.023
6-second.....	16.83	.045	.055	.050	.025
1-minute.....	19.25	.082	.087	.084	.042
5-minute.....	19.99	.111	.063	.087	.043
10-minute.....	16.48	.189	.158	.173	.087
1-hour.....	18.40	.206	.186	.197	.098
2-day.....	27.22	.308	.282	.295	.148
2-week.....	23.17	.58	.69	.633	.316
Direct-current.....	9.82	.85850

As mentioned earlier, it will be seen that the pilot-specimen loss is quite large and that there is considerable variation under the different frequencies. This is evidently a real variation due to a difference in soil action, because it was found that in individual cases when the pilot-specimen corrosion varied considerably from the average the current-carrying electrodes would also vary in the same direction. The coefficient of corrosion only in the case of the 60-cycle tests is negative. The electrodes were numbered consecutively, an odd number and a succeeding even number being grouped in each cell. The difference in the coefficient of corrosion between the odd and even electrodes is rather large in some cases; for example, in the 5-minute specimens the coefficient is 0.116 for the odd electrodes and only 0.065 for the even, and in the 15-cycle test the per cent discrepancy is large, although the values in grams do not differ greatly. The direct-current test shows a coefficient of only 0.85, which is rather low, and this can only be explained as being probably due to the effect of the iron oxide serving as a protection rather than accelerating the corrosion. The next to the last column is simply double the one succeeding or an average of the odd and even electrode coefficients.

(b) **Indoor Tests—Iron Electrodes in Soil with Sodium Carbonate.**—In Table 6, containing the results on iron electrodes in sodium carbonate soil, it will be noted that in the case of the 60-cycle run the coefficient of corrosion is positive but that the values in the other cases of reverse currents are smaller than in the natural soil. In the 2-week test the odd-electrode loss is considerably less than the even, supporting the theory that in these longer time reversals the electrodes which are positive last suffer the greater loss. Under these conditions the direct-current loss is very nearly 100 per cent.

TABLE 6

Summary of Alternating Current Electrolysis Tests—II

[Variable, frequency of reversal; indoor tests; iron electrodes; soil and sodium carbonate electrolyte]

Period of cycle	Total loss			Electrolytic loss		
	Odd electrodes	Even electrodes	Pilot	Odd electrodes	Even electrodes	Average
	Grams	Grams	Grams	Grams	Grams	Grams
60-cycle.....	1.390	1.373	1.199	+0.191	0.174	+0.182
1-second.....	.865	1.146	.677	.188	.469	.329
10-minute.....	1.617	1.532	.835	.782	.679	.739
2 week.....	7.922	9.081	1.636	6.286	7.451	6.868
Direct-current.....	10.423	.172	.819	9.604

TABLE 6—Continued

Summary of Alternating Current Electrolysis Tests—II—Continued

Period of cycle	Current dis-charge (amp. hours)	Coefficient of corrosion			
		Odd elec-trodes	Even elec-trodes	On basis of anodic current	On basis of total current
60-cycle.....	16.05	0.023	0.021	0.022	0.011
1-second.....	17.99	.020	.050	.035	.018
10-minute.....	16.48	.091	.081	.086	.043
2-week.....	23.17	.52	.62	.57	.285
Direct-current.....	9.82	.9494

(c) **Indoor Tests—Lead Electrodes in Soil.**—With lead electrodes in soil very regular results were obtained. In Table 7 the loss is shown to be increasing gradually from 60 cycles to 2 weeks with only one discrepancy, the loss on the even electrode (see p. 24) in 2-day reversals being considerably smaller than on the 10-minute and 1-hour specimens. The products of corrosion seem to be increasing the effect on the pilot specimens, as it will be noted that the loss is increasing as the frequency decreases. However, the most remarkable facts concerning these tests is that the odd electrodes, those which were initially positive in the tests, lost considerably more than the even electrodes in both the 2-day and 2-week test. The other remarkable feature is the small coefficient of corrosion exhibited in the case of the direct-current test. Since in the first set weighed the losses were so small (only 22 per cent of the theoretical), a second run was made and a coefficient of 25.4 per cent obtained, practically the same as before. This indicates that under the conditions of these tests and probably under most soil conditions the corrosion of lead is very considerably less than it has been formerly considered to be.

TABLE 7

Summary of Alternating-Current Electrolysis Tests—III

[Variable, frequency of reversal; indoor tests; lead electrodes; soil electrolyte]

Period of cycle	Total loss			Electrolytic loss		
	Odd elec- trodes	Even elec- trodes	Pilot	Odd elec- trodes	Even elec- trodes	Average
	Grams	Grams	Grams	Grams	Grams	Grams
60-cycle.....	0.325	0.328	0.124	+0.201	+0.204	0.202
15-cycle.....	.342	.332	.133	.209	.199	.204
1-second.....	.385	.354	.118	.267	.236	.252
6-second.....	.518	.528	.098	.420	.430	.425
1-minute.....	2.860	2.845	.652	2.208	2.193	2.200
5-minute.....	3.868	3.634	.406	3.462	3.228	3.345
10-minute.....	3.468	3.738	.341	3.127	3.397	3.262
1-hour.....	5.886	5.771	.901	4.985	4.870	4.928
2-day.....	8.719	5.072	1.357	7.362	3.715	5.538
2-week.....	13.710	7.789	1.176	12.634	6.713	9.674
Direct-current.....	12.319937	11.382	11.382
Do.....	13.574882	12.692

Period of cycle	Current dis- charge (amp. hours)	Coefficient of corrosion			
		Odd elec- trodes	Even elec- trodes	On basis of anodic current	On basis of total current
60-cycle.....	16.05	0.0065	0.0066	0.0065	0.0033
15-cycle.....	13.32	.0082	.0077	.0080	.0040
1-second.....	14.87	.0093	.0082	.0088	.0044
6-second.....	16.83	.0129	.0132	.0131	.0065
1-minute.....	19.25	.059	.059	.059	.030
5-minute.....	19.99	.089	.085	.086	.043
10-minute.....	14.95	.108	.118	.112	.056
1-hour.....	18.40	.140	.137	.139	.069
2-day.....	27.22	.140	.071	.105	.053
2-week.....	23.17	.282	.150	.216	.108
Direct-current.....	13.40	.220220
Do.....	12.93	.254254

(d) Indoor Tests—Lead Electrodes in Sodium Carbonate.—The losses of lead electrodes in sodium carbonate (Table 8) are greater than in the normal soil, the difference being especially noticeable in the longer reversals and in the direct-current tests. For example, in the weekly reversals the coefficient of corrosion in normal soil was 0.108 while in the sodium carbonate it was 0.172; the direct-current coefficient of corrosion has risen from about 25 per cent to 34 per cent.

TABLE 8

Summary of Alternating-Current Electrolysis Tests—IV

[Variable, frequency of reversal; indoor tests; lead electrodes; soil and sodium carbonate electrolyte]

Period of cycle	Total loss			Electrolytic loss		
	Odd elec- trodes	Even elec- trodes	Pilot	Odd elec- trodes	Even elec- trodes	Average
	Grams	Grams	Grams	Grams	Grams	Grams
60-cycle.....	0.555	0.542	0.077	0.478	+0.465	0.471
1-second.....	.316	.630	.062	.254	.568	.411
10-minute.....	4.019	3.844	.110	3.909	3.734	3.822
2-week.....	17.356	13.487	.111	17.245	13.370	15.307
Direct-current.....	17.726075	17.651	17.651

Period of cycle	Current dis- charge (amp. hours)	Coefficient of corrosion			
		Odd elec- trodes	Even elec- trodes	On basis of anodic current	On basis of total current
60-cycle.....	16.05	0.0154	0.0150	0.0152	0.0076
1-second.....	14.87	.0088	.0198	.0143	.0071
10-minute.....	14.95	.135	.129	.132	.066
2-week.....	23.17	.386	.299	.344	.172
Direct-current.....	13.4	.340

(e) **Outdoor Tests—Iron and Lead Electrodes in Soil.**—The outdoor tests shown in Table 9 are not extensive, but the cases given show reasonably good agreement with the indoor tests given above. The coefficient of corrosion at 60 cycles is slightly less than 0.01 for iron electrodes and the direct-current loss is 0.70. Considering only the direct-current tests on iron, it was noted that as the voltage necessary to maintain the current at 0.5 milliampere per square centimeter became greater the coefficient of corrosion decreased. For example, we find a coefficient of corrosion of 0.96 for iron electrodes in sodium carbonate soil and 0.85 in normal soil on the indoor tests and only 0.70 for the outdoor tests and the potential has varied from about 10 volts on the first to 35 on the last test.

TABLE 9

Summary of Alternating Current Electrolysis Tests—V

[Variable, frequency of reversal; outdoor tests; iron and lead electrodes; soil and sodium carbonate electrolyte]

Period of cycle	Total loss			Electrolytic loss		
	Odd elec-trodes	Even elec-trodes	Pilot	Odd elec-trodes	Even elec-trodes	Average
	Grams	Grams	Grams	Grams	Grams	Grams
60-cycle.....	2.65	2.60	0.97	1.68	1.63	1.65
1-second.....	9.06	7.30	5.94	3.12	1.36	2.24
Direct-current.....	41.96	1.73	4.61	37.35	37.35	37.35
Do.....	871.86		6.22	865.64		865.64
						Lead

Period of cycle	Current dis-charge (amp. hours)	Coefficient of corrosion			
		Odd elec-trodes	Even elec-trodes	On basis of anodic current	On basis of total current
60-cycle.....	165.4	0.0203	0.0197	0.0192	0.0096
1-second.....	102.0	.0589	.0256	.0431	.0215
Direct-current.....	51.6	.700	.700	.700	.700
Do.....	1034.0		.217	.217	.217
					Lead

8. CURVES

The data shown in the above tables have been plotted in curves in which the ordinates are coefficients of corrosion expressed in per cent and the abscissas are the logarithms of the number of seconds required for one complete cycle. Fig. 4 shows the data obtained with iron electrodes, this being based on the average electrode loss and the total current flowing in any one direction through the cells. The coefficient is therefore based on the total current discharged by one electrode. It will be noted that the curve for the coefficient in natural soil is above that for soil containing sodium carbonate, except the last point for direct current, when the latter shows the greater loss. The values begin to rise quite rapidly at about the 10-minute cycle, and reach a maximum in the direct-current test, the value for which is placed arbitrarily as far as the time is concerned. It is very interesting to note that even in the case of a cycle of two weeks' duration the coefficient of corrosion is only about 0.6 and on a two-day cycle only 0.3 of its value for direct current.

Fig. 5 contains the same data on lead electrodes, and here it is seen that the soil containing sodium carbonate produces a consistently higher coefficient of corrosion than the natural soil, just the reverse of the condition with iron electrodes. The tendency to rise is noticed at an earlier point or a higher frequency than with the iron, beginning with about the one-minute cycle, and at a cycle

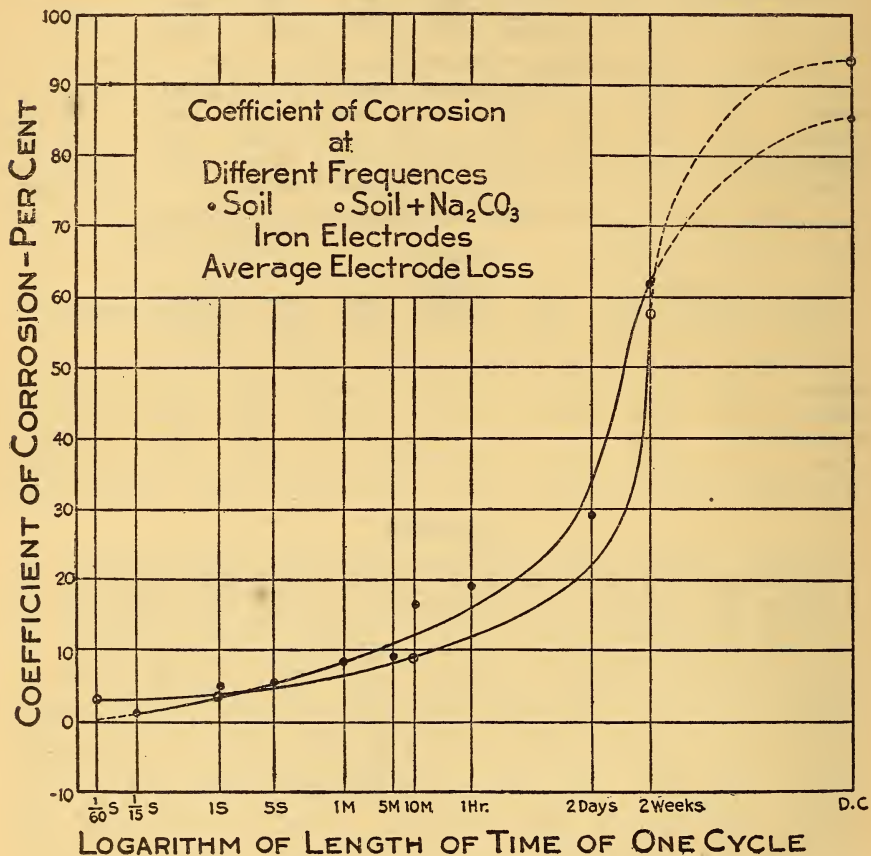


FIG. 4

of two weeks' duration the coefficient of corrosion has reached the same value as for direct current.

9. SUPPLEMENTARY TESTS

Since certain authors have pointed out the fact that the wave form of alternating current is affected when passing through an electrolytic cell, and since a material change in such wave form would affect the current measurements, an oscillograph was used

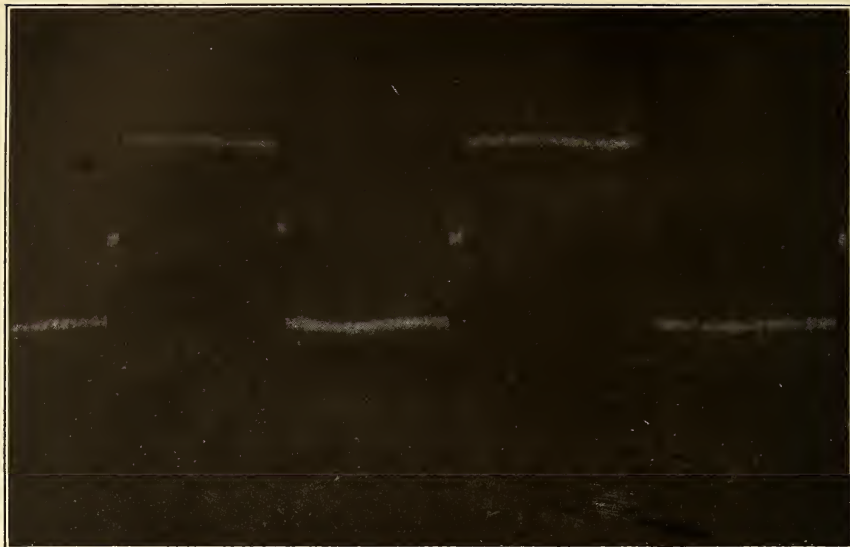


FIG. 6.—*Wave shape for one-second cycle*

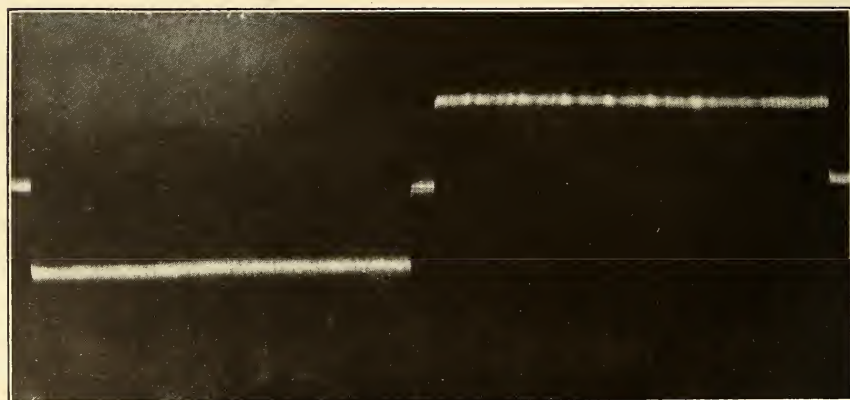


FIG. 7.—*Wave shape for six-second cycle*

to determine the wave form of current passing through the cell and its relation to the potential wave impressed on it. It was found that there was no appreciable distortion of the wave shape due to the presence of the cell.

In order to determine the cycle of operation of the commutating machine exactly, the current wave was observed with the oscillograph. It is seen that on the one-second cycle (Fig. 6)

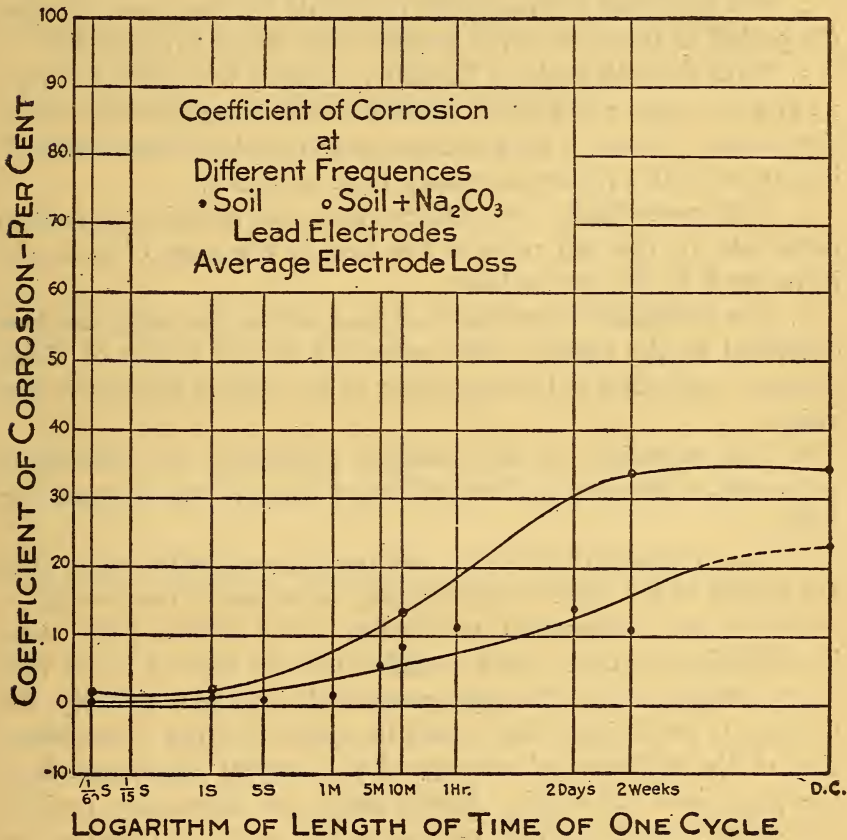


FIG. 5

the current increases slightly during about the first one-fourth second and falls during the remainder of the half cycle. In the six-second cycle (Fig. 7) this rise and fall is seen, and the fall continues for a considerable part of each half cycle, but the waves appear to be so nearly flat top in both the one-second cycle and the six-second cycle that no correction due to the variation between the average value and the effective value need be made.

III. CONCLUSIONS

From the above results certain conclusions may be drawn concerning the corrosion of iron and lead electrodes under usual soil conditions when exposed to the action of periodically reversed current.

1. The corrosion of both iron and lead electrodes decreases with increasing frequency of reversal of the current.

2. The corrosion is practically negligible for both metals when the period of the cycle is not greater than about five minutes.

3. With iron electrodes a limiting frequency is reached between 15 and 60 cycles per second, beyond which no appreciable corrosion occurs. No such limit was reached in the lead tests, although it may exist at a higher frequency than 60 cycles.

4. With periodically reversed currents, the addition of sodium carbonate to the soil reduces the loss in the case of iron and increases it in the case of lead.

5. The coefficient of corrosion of lead, under the soil conditions described in the report, when subjected to the action of direct current, was found to be only about 25 per cent of the theoretical value.

6. The corrosion of lead reaches practically the maximum value with a frequency of reversal lying between one day and one week.

7. The corrosion of iron does not reach a maximum value until the period of the cycle is considerably in excess of two weeks.

8. The most important conclusion to be drawn from these investigations is that in the so-called neutral zone of street railway networks, where the pipes continually reverse in polarity, the damage is much less than would be expected from a consideration of the arithmetical average of the current discharged from the pipes into the earth. Where pipes are alternately positive and negative with periods not exceeding 10 or 15 minutes, the algebraic sum of the current discharged is more nearly a correct index to the total damage that will result than any other figure than can readily be obtained.

9. The reduction in corrosion due to periodically reversed currents appears to be due to the fact that the corrosive process is in a large degree reversible; so that the metal corroded during the half cycle when current is being discharged is in large measure redeposited during the succeeding half cycle when the current flows toward the metal. This redeposited metal may not be of

much value mechanically, but it serves as an anode surface during the next succeeding half cycle, and thus protects the uncorroded metal beneath.

10. The extent to which the corrosive process is reversible depends upon the freedom with which the electrolyte circulates, and particularly on the freedom of access of such substances as oxygen or carbon dioxide, which may result in secondary reactions giving rise to insoluble precipitates of the corroded metal. It is largely for this reason that the corrosion becomes greater with a longer period of the cycle, since the longer the period the greater will be the effect of these secondary reactions.

WASHINGTON, February 14, 1916.



